MANUAL OF METAL-TO-CERAMIC SEALING TECHNIQUES

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ELECTRONIC TUBE DIVISION

SPERRY GYROSCOPE COMPANY
DIVISION OF SPERRY RAND CORPORATION
GREAT NECK, NEW YORK

Prepared by

ENGINEERING DEPARTMENT
C.W. Johnson

PUBLICATIONS DEPARTMENT
E.W. Cheatham

DDC

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SECTION I

INTRODUCTION

Metal-to-ceramic seals have been in existence for thousands of years, since early man first made decorative enamel-copper trinkets. Little progress was made until the nineteenth century with the advent of the internal combustion engine and the need for spark plugs. Since then, there have been considerable technological advances, particularly with regard to the electronic tube industry. To further knowledge in this area, the Electronic Tube Division of Sperry Gyroscope Company conducted a seal technology study for the Rome Air Development Center, Air Force Systems Command, under Contract No. AF30(602)-2371. This manual, discussing the procedures to fabricate metal-to-ceramic seals, is based on the study program.

During the study program, the effects known variables had upon the ultimate strength of metal-to-ceramic seals were investigated. Five statistically designed experiments were performed to examine the significance of the variables and their interactions on over-all seal strength. The results of the program were masked to a great extent by a high residual error due to uncontrolled and/or unknown variables; only the most marked effects could be observed and assigned statistical significance.

Because of the high coefficients of variation (or dispersion) of the experiments, many of the recommended processes are of an advisory nature, rather than of specific scientific preciseness. The main contribution of this manual is in cataloging the variety of processes required to fabricate metal-to-ceramic seals, with recommendations as to the relative degrees of importance in controlling various phases of the operations. Some of the techniques employed in fabricating seals and controlling the known variables are described; the ceramic engineer can select those suitable for his particular needs. It must be remembered, however, that fabrication of seals depends to a large extent upon the skills of the operators; and reproducibility and reliability can be gained only through proper training and practice.

The organization of this manual is patterned after the normal work flow, from raw materials to finished product:

- Selection of raw materials

- Seal design

- Parts preparation and metallizing

- Fixtures and assembly

- Brazing

- Control testing

- Failure analysis.

It must be emphasized that this manual provides recommendations and not absolute instructions. With the large variety of ceramics and metallizing mixtures available, an almost infinite number of combinations is possible, each possessing individual characteristics. It is true that many combinations with similar characteristics can be grouped together, but proficiency in the use of a particular ceramic-metallizing combination is obtained through careful observation of all phases of the operation.

Many techniques which can be employed in the processing steps have not been mentioned for the sake of brevity. Substitutions can be made because of available equipment and facilities. For instance, if electroplating facilities are not available, the application of nickelous oxide or cuprous oxide, with subsequent reducing atmosphere sintering, can replace the electroplated layers. Similarly, some electroless platings can be used if phosphorous contamination is permissible. The ceramic engineer must select several combinations of ceramic, metallizing, metal members, and brazing materials and then work with these to establish basic parameters of operation. A skilled engineer soon develops a basic understanding of his selected combinations, and is better able to employ these materials for his purposes.

Considerable work still remains to determine the basic mechanisms involved in these processes. Several investigators have hypothesized the mechanisms, but none has succeeded in accurately describing the observed

phenomena. Manufacturing of metal-to-ceramic seals currently straddles the line between science and skilled craft; a few years ago it was completely craft. The immediate future should benefit as more scientific data are collected, as the mechanisms are more completely understood.

SECTION II

SELECTION OF RAW MATERIALS

2-1. CERAMICS

The choice of the ceramic body is basic to the process of sealing. Selection is primarily determined by the application of the device in which the seal is incorporated, because of the mechanical and electrical properties of different ceramics. Some of the properties to consider are thermal shock resistance, r-f losses, softening temperature, thermal expansion, porosity or vacuum-tightness, degassing, and physical strength.

The percentage of alumina in the body is proportional to the ease of sealing. Many ceramics from a variety of suppliers are available covering a range from 85- to 100-percent alumina. Dense vacuum-tight aluminas are made by mixing a small percentage of the vitreous or glassy material referred to as a flux with the refractory polycrystalline material, and heating the composition beyond the melting point of the flux. Two alumina bodies with the same percent alumina content will not necessarily have the same physical and electrical properties, because the composition of the flux can vary. In general, ceramics increase in price as the purity of alumina increases. The

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lowest-purity alumina which will be satisfactory provides the greatest cost savings in raw material and yield in processing.

2.2. METALS

The selection of the metal member of the seal is somewhat governed by the physical and electrical requirements, but it is more dependent upon the ceramic body chosen. Characteristics such as magnetic properties, r-f and d-c conductivity, and structural strength determine the selection of a group of metals. A particular metal member is then selected on the basis of its coefficient of expansion. Ideally, the ceramic and the metal should be identically matched, so that they expand and contract at the same rate throughout the brazing and operating cycles; stresses caused by dissimilar expansion characteristics are thereby eliminated. It should be noted that the stringent thermal cycling tests performed to evaluate the reliability of finished seals are based on the stresses developed between the dissimilarly expanded ceramic and metal members.

Expansion coefficients of some typical ceramic bodies and some of the metals more commonly employed in sealing to the ceramics are shown in figure 1. No ideal combinations are presently available, but the metals and ceramics currently used allow construction of highly reliable seals. Some of the metals

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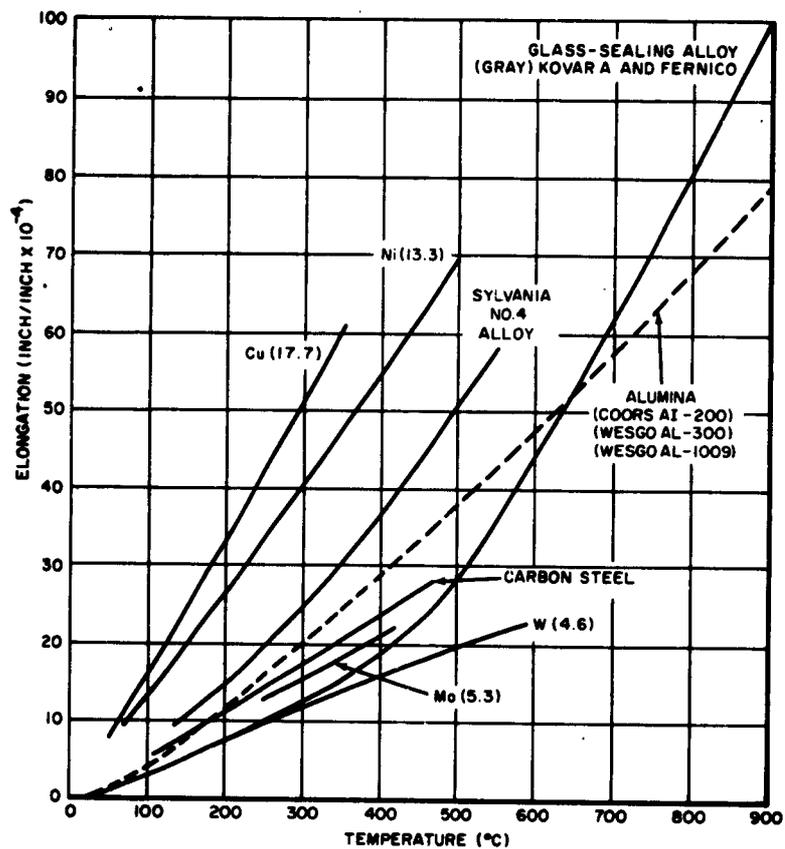
FIGURE I. EXPANSION COEFFICIENTS OF TYPICAL
CERAMIC BODIES AND METALS

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normally encountered in fabricating the
variety of seals described in Section III are
Kovar, No. 42 alloy, Sylvania No. 4, nickel,
molybdenum, and copper.

SECTION III

SEAL DESIGN

3-1. BASIC THIN-WALL OD COMPRESSION SEALS

The thin-wall OD compression seal (figure 2) employs a thin surrounding metal member which relies on its compliance to compensate for the mechanical stresses caused by the thermal expansion mismatch. Wall thickness usually ranges from 0.005 inch to 0.025 inch. The metal member should be as thin as possible while still offering the mechanical strength required for handling and processing.

In designing this type of seal, the engineer must rely heavily on judgment and previous experience. Small seals—those about 0.25 inch and less in diameter—are more difficult to seal successfully than are seals having, for example, a diameter of 1 or 2 inches. Wherever possible, small seals should use thinner metals. Seal thickness or length is an important factor. Extremely thin ceramic members, which provide short leak paths, are to be avoided wherever possible. Seals having thicknesses or leak distances of 0.125 inch or greater offer fewer problems than those in the 0.050- to 0.030-inch range. In designing seals, it is necessary to allow proper clearance between the ceramic and metal member

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ROOM
TEMPERATURE

HEATED

MISMATCH
STRESS
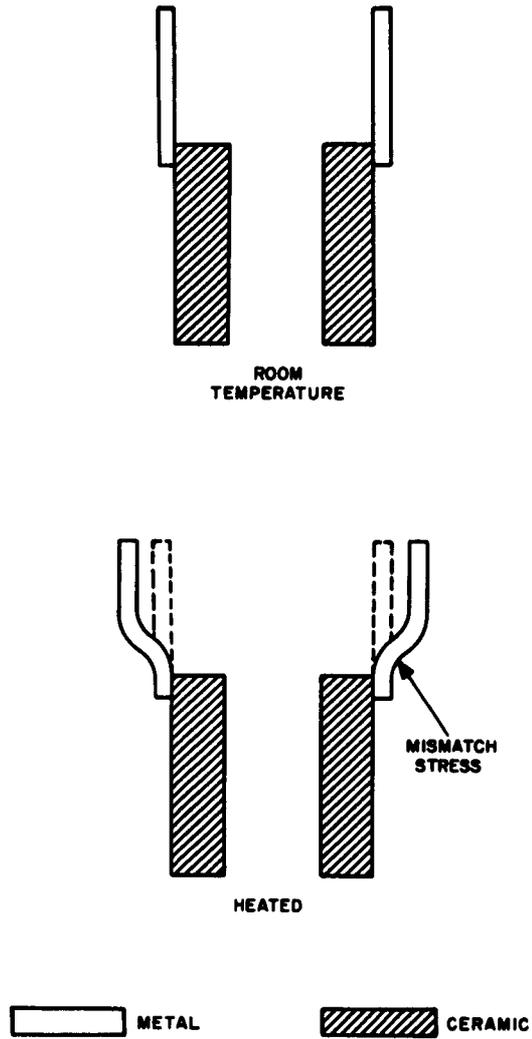
METAL   CERAMIC

FIGURE 2.   THIN-WALL OD COMPRESSION SEAL

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for the application of the metallizing and plating. Basic rules for allowances are given in Appendix A.

When sealing a ceramic assembly to a massive metal member, a transition metal of thinner cross section or a thinned-down metal similar to the massive metal member can be employed (figure 3). The transition metal is then selected to match with the alumina body; the massive metal member can be any material to which the transition metal can be joined.

Thin-wall OD compression seals should be designed to be self-jigging to facilitate manufacturing. This is accomplished by incorporating a shoulder to position the ceramic and metal with respect to each other (figure 4). The step or shoulder should not be part of the ceramic because of the extra expenses involved.

3-2. ID OR PIN SEALS

The pin material dictates the seal design to a large extent. If the pin is made of lower-expansion molybdenum, it is usually solid. With nickel, copper, or other higher-expansion metals, the pins are usually hollow to allow more compliance so that the metal can yield to the mismatch.

Wall thickness usually varies from 0.005 inch to about 0.015 inch, but can be made larger for very large ID holes. In general, the total wall thickness should not exceed 20 percent of

CERAMIC

HEAVY METAL
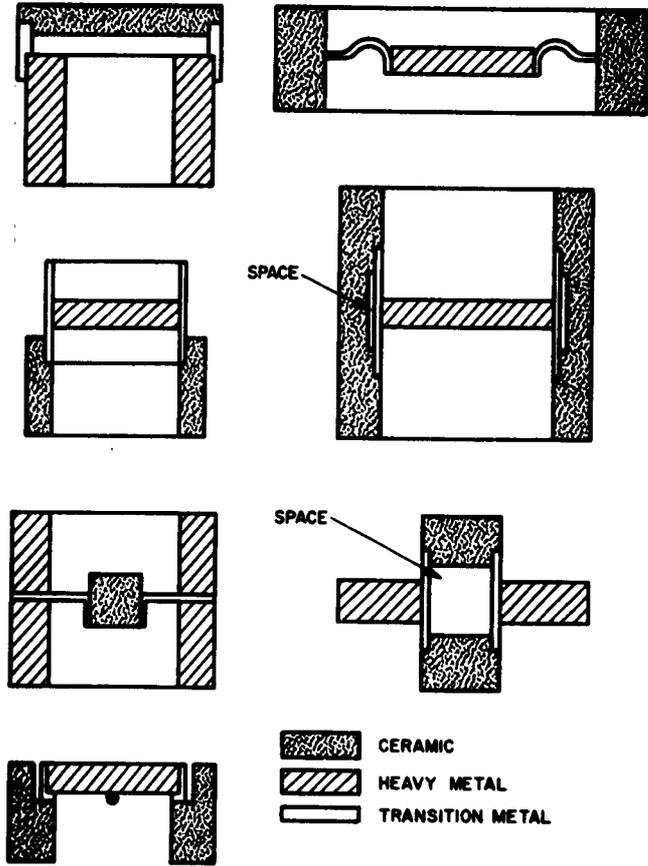
TRANSITION METAL

FIGURE 3.   TRANSITIONS TO THICK-WALL
METAL MEMBERS

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the diameter of the ceramic hole, following the rule that the metal member should be as thin as possible. When tubular pin material is employed, plugs can be welded or brazed at both ends of the tubing to produce a vacuum-tight seal. For high current-carrying capabilities, a center conductor with proper clearance can be employed; brazing should be at both ends of the compliant metal tubing (figure 5).

3-3. BUTT SEALS

Butt seals are desirable because of the ease of assembly. The mating surfaces can be easily and inexpensively ground flat; metallizing procedures include silk screening, roller coating, and spraying with simple fixtures and jigging. Typical butt-seal assemblies are illustrated in figure 6.

The transverse loading stress, normally encountered in horizontally supported tubular devices, will peel simple butt seals more readily than the more physically rugged compression seal. Back-up ceramic rings have been used to reduce the thermal expansion mismatch sheer stresses, and consequently increase the reliability of the seals (figure 7).

Nickel is frequently used, although Kovar is employed where more strength is required. As ductile and thin a metal as possible should be used. Seal leak paths should be at least 0.125 inch for a safe low working limit. The

13
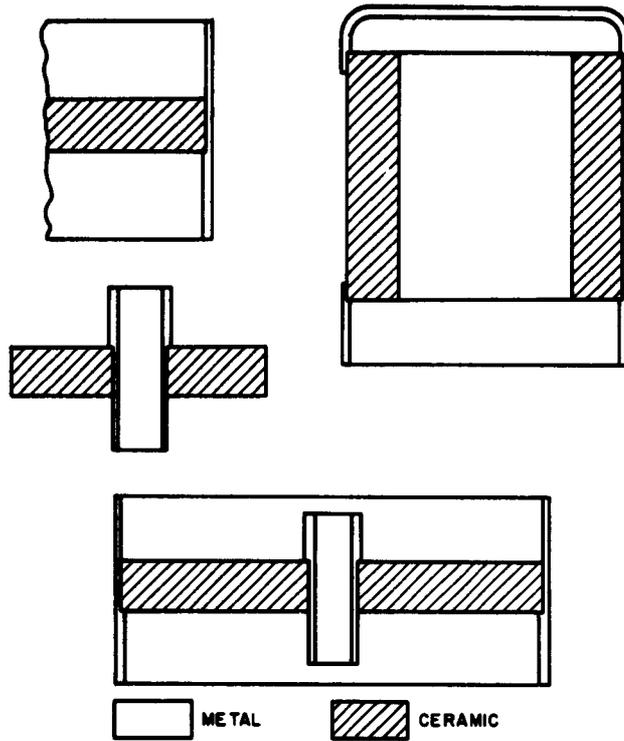
METAL   CERAMIC

FIGURE 4.   SELF-JIGGING SEALS IN WHICH METAL
MEMBER PERFORMS JIGGING
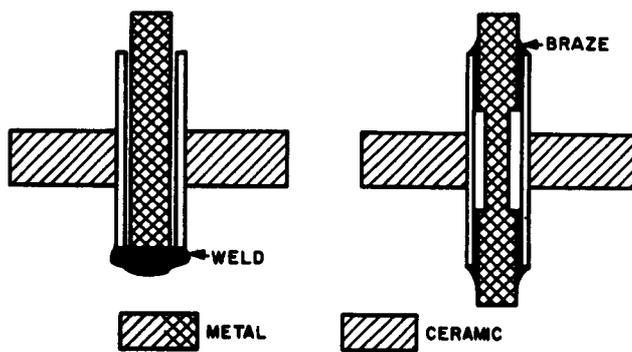
METAL   CERAMIC

FIGURE 5.   HOLLOW-PIN SEALS STRENGTHENED WITH
SOLID PIN INSERT

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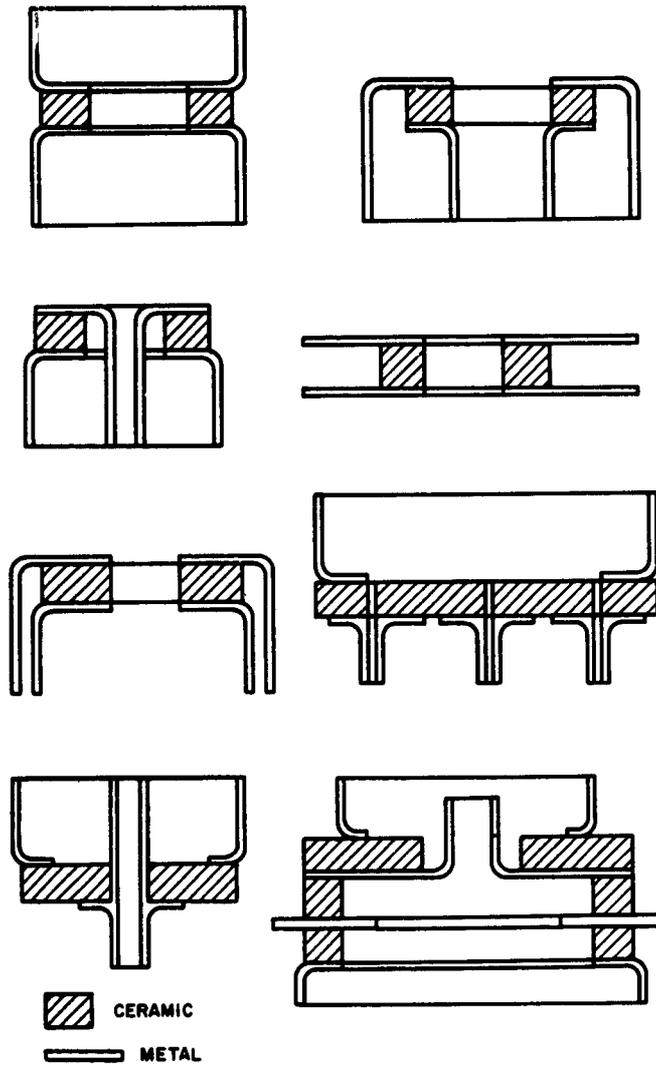
FIGURE 6. TYPICAL BUTT-SEAL ASSEMBLIES

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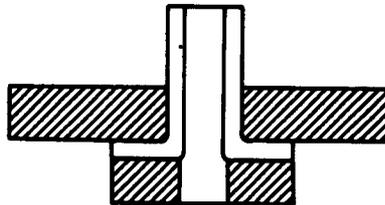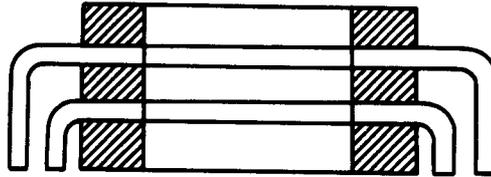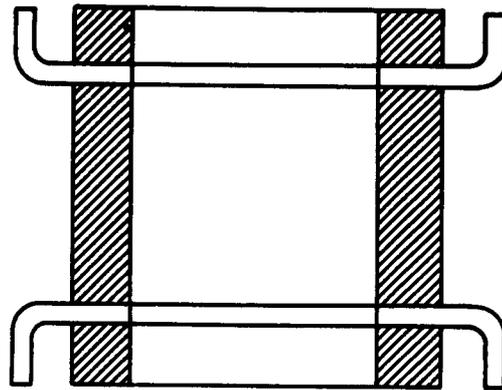
CERAMIC

METAL

FIGURE 7.   BACK-UP OF DUCTILE METAL SEAL
WITH SECOND OR BLANK CERAMIC

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thickness of the metal should be the same order of magnitude as with the OD compression seal. In the special case in which two metallized ceramics are fabricated into a vacuum-tight joint, a spacing material of 0.010- or 0.020-inch nickel is normally employed between the ceramics to minimize stresses.

3-4. NONSTANDARD SEALS

Some typical nonstandard seals are illustrated in figures 8 and 9. Figure 8 shows a thick-wall seal employed for windows and similar types of dielectrics. Rectangular seals, which can be sealed into thin- or thick-wall metal members, are shown in figure 9. Rectangular ceramic pieces should have substantial radii of no less than 0.030 to 0.040 inch because the metallizing of square corners is extremely difficult and leads to stress concentrations in the finished seals.

METAL   CERAMIC

FIGURE 8.   THICK-WALL SEAL

METAL   CERAMIC SLAB   WAVEGUIDE
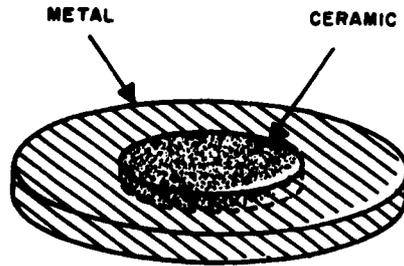
CERAMIC

WINDOW SEAL   WAVEGUIDE SEAL
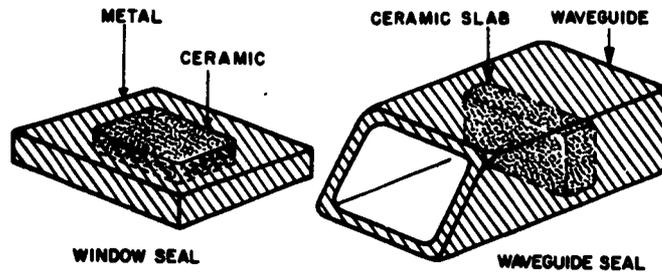
FIGURE 9.   RECTANGULAR SEALS

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SECTION IV

PARTS PREPARATION AND METALLIZING

4-1. CLEANING OF CERAMICS

After the ceramic and metal members
have been selected and the seal has been
designed, the parts must be prepared for met-
allizing and electroplating prior to assembly.
Ceramics received from the suppliers contain
organic and (occasionally) metallic contaminants
on the surface of the body. These must be com-
pletely removed so as not to interfere with the
metallizing operations. The ceramic parts
are placed in a clean Pyrex container in which
all chemical cleaning is performed. The parts
must not be handled with metallic utensils.

The ceramic parts are boiled in clean
concentrated nitric acid (CP grade) for 30
minutes. The nitric acid solution is then de-
cantered, and the parts flushed with clean dis-
tilled or deionized water. * The parts are then
boiled for 10 minutes in fresh deionized water,
followed by a flush with clean, cold deionized
water. Ultrasonic rinsing in cold deionized
water as a final rinse is recommended, but not

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*Distilled water can be substituted for deionized
water, whenever specified.

absolutely necessary. After all water rinses, the ceramic parts are rinsed in methanol (CP grade) in the same Pyrex container.

After decantering the excess methanol, the Pyrex beaker containing the ceramics is dried in an air oven at 120°C. The parts are then placed on a clean ceramic plate, previously air-fired, and the plate and parts are air-fired at 1000 ± 25°C for 10 minutes; care must be taken to raise and lower the temperature at a rate which will avoid thermal shock and cracking of the ceramic pieces. After cooling, the parts are placed in clean polyethylene bags and stored until ready for metallizing. A maximum of 3 days can elapse between cleaning and metallizing of the ceramics; if this time is exceeded, air-firing is recommended to remove accumulated organic contamination.

The clean ceramic parts must be handled with clean rubber finger cots and/or plastic-coated nylon gloves to prevent finger oils and other contaminants from being transferred to the ceramic surfaces. Organic materials, such as finger oils, which are allowed to remain on the ceramics during subsequent operations are reduced to carbon, and metallic salts are reduced to metals and metal oxides; these stain the ceramics and cause sparking, electrical leakage, and r-f losses in many applications. Tweezers, spatulas, and other tools used in handling the ceramics must be ceramic or plastic coated.

4-2. CLEANING AND PLATING OF METALS

Metal parts require cleaning similar to that of ceramics to produce satisfactory seals. Nickel, monel, Kovar, and stainless steel receive the following treatment. The metal parts are ultrasonically cleaned in trichloroethylene, followed by a hot tap-water rinse and a concentrated hydrochloric acid pickle long enough to eliminate scale and oxides. This is followed by a cold tap-water rinse, and then a cold deionized water rinse. A methanol dip, similar to the ceramic drying procedure, followed by oven drying at 120°C prepares the part for further processing.

All metal parts generally require metal plating. A copper flash is also required in the regions to be brazed; this prewets the joint areas, allowing the brazing material to flow more readily. The plating serves different purposes for the various materials (nickel is not plated). Molybdenum is plated to assist in the wetting by the solder. Stainless steel is afforded protection against oxidation during brazing in the wet reducing atmosphere. Kovar is plated to prevent intergranular penetration during brazing with silver-containing alloys, and also to protect against oxidation during storage.

4-3. METALLIZING

The cleaned ceramics are now ready for the application of the metallizing mixture. Typical mixtures are listed in Appendix B.

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There are several techniques of applying the metallizing (figures 10, 11, and 12); the one chosen depends on the specific requirements. Metallizing thickness does not appear to have a large significance in seal strength, but does cause some variations. Therefore, efforts to standardize the procedure will result in a more controlled and reproducible process, in addition to enabling tighter dimensional tolerances to be maintained for easier fits during the assembly stages.

Handpainting with a sable brush is the most commonly employed method for small lots and oddly shaped pieces. Wherever possible, the part to be coated should be mechanically rotated so that the total seal area can be coated uniformly before the mixture dries. This prevents nonuniformity of thickness in the seal area and guarantees freedom from voids. Spray coating and roller coating require masking and more fixtures; thus, they are suitable for large production runs. The viscosity of the mixture determines, to some extent, the ease of application and the resultant thickness and uniformity; it should be maintained at a constant value. As the mixture is used, evaporation reduces the amount of solvent. With time, the mixture becomes more viscous, requiring periodic replacement from the stock bottle. In no case should any unused portion of metallizing mixture be returned to the stock mixture, as this will cause variations in content and viscosity.

FIGURE 10.   HAND-COATING EQUIPMENT

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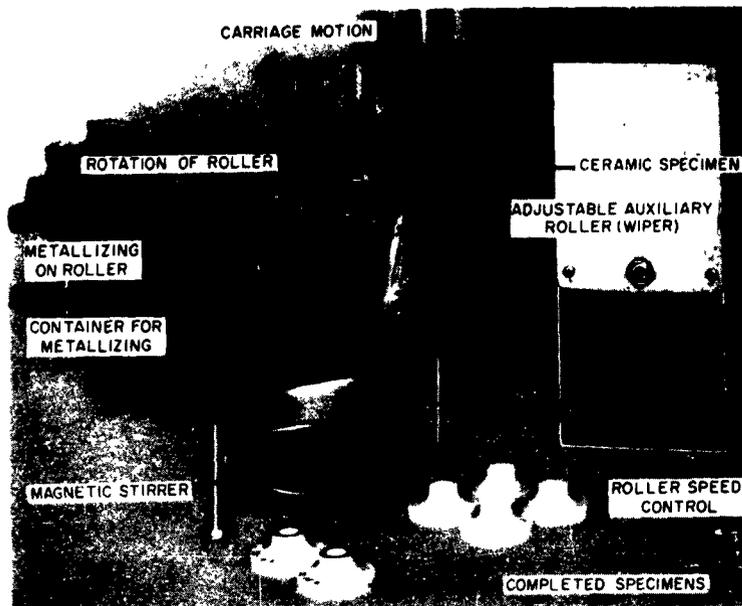
FIGURE 11. ROLLER-COATING EQUIPMENT
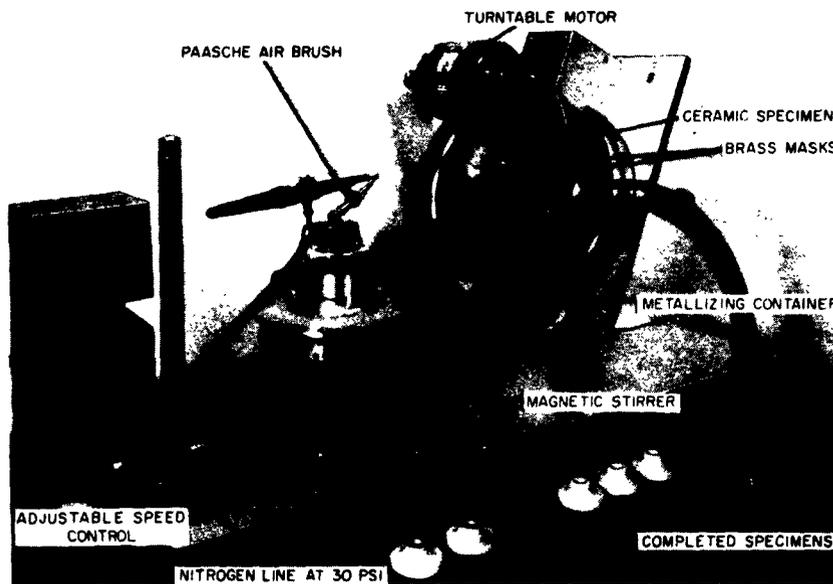
FIGURE 12. SPRAY-COATING EQUIPMENT

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After the ceramics have been coated, it is essential that the solvents be completely evaporated before sintering; otherwise, there will be explosive expulsion of the materials during sintering, with subsequent damage to the coated surface. The ceramics are then placed in clean molybdenum boats, or for large assemblies on corrugated molybdenum sheets or mesh screening lining the bottom of the boat. (The coated ceramics can be placed temporarily on lint-free tissue before being placed in the boats.) The corrugated metal and screening reduce the thermal path between the ceramic and the bottom of the boat resting in the hot zone of the furnace, thereby minimizing temperature shock conditions which can damage or destroy the ceramic. The parts are positioned to prevent the relatively soft, unsintered metallized coating from rubbing onto unmetallized surfaces.

The ceramics are then placed in the furnace for sintering. The type of furnace employed governs the particular procedure. For periodic batch furnaces, the ceramics are normally protected against thermal shock by the thermal inertia of the furnace, which acts as the limiting heat rate to which the parts are subjected. A pusher, or horizontal, furnace through which the boat is passed must be handled with extreme precaution to minimize shocking the ceramics; several progressive steps moving the boat closer to the hot zone, finally into the hot zone, followed by graded movements into the cooling chamber are

required to protect the pieces. The furnace atmosphere can be forming gas, dissociated ammonia, or pure hydrogen; but in all cases the dewpoint of the gas must be maintained at a level no less than 30°C. As long as the minimum dewpoint is maintained, the seal strength is not drastically affected.

Measurement of dewpoint in the region of 30°C warrants description. The dewpoint cup employed (figure 13) consists of a closed chamber (with a glass viewing window) through which the sample gas is passed, and a projecting polished chrome-plated cup upon which the gas impinges. Hot water at approximately 55°C (after the chamber is purged for at least 15 minutes at a flow rate of approximately 2 cfh) is placed in the metal cup. Observing the polished surface of the cup, which is immersed in the sample gas of the chamber, a thermometer of the proper dewpoint range is used to stir the hot water while small amounts of cold water are added. This procedure is followed until a blush forms on the metal cup, at which time the thermometer is read. This temperature is the dewpoint of the sampled gas. It is necessary to keep the sampling tubes and lines above the temperature of the dewpoint (30°C). Otherwise, the cooler walls of the sampling tube will condense out the water vapor, effectively reducing the sample gas dewpoint and giving an incorrect indication of the actual dewpoint in the furnace.
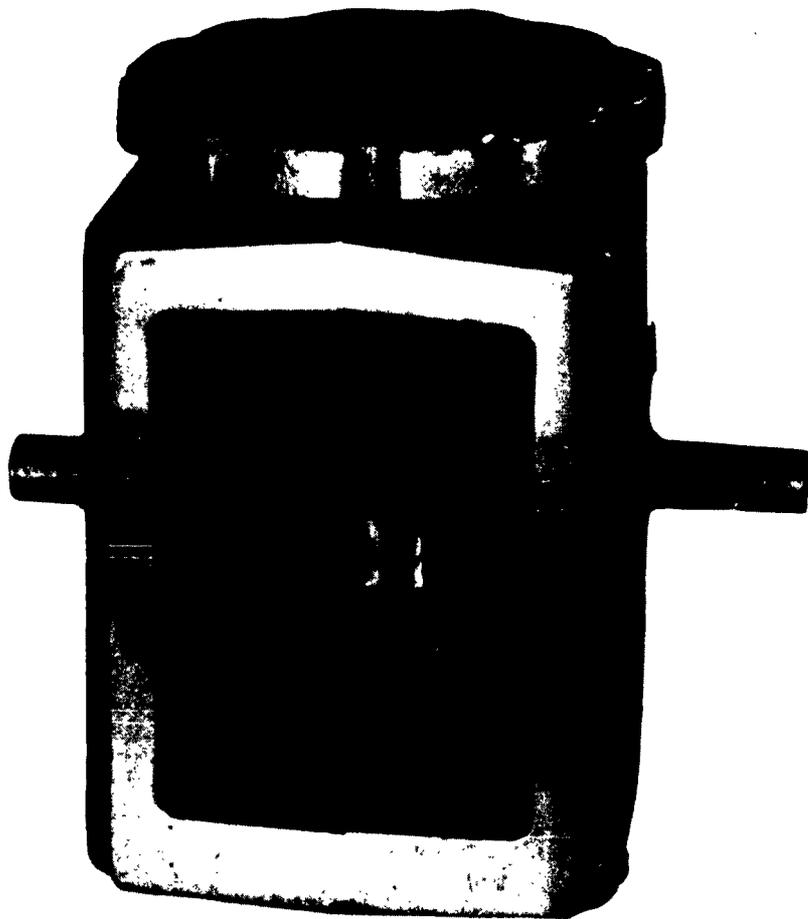
FIGURE 13.   DEWPOINT CUP

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The temperature of sintering and the soak time at the sintering temperature vary for the combination of ceramic body and metallizing mixture. Some recommended combinations of ceramic body, metallizing mixture, and sintering cycle are listed in Appendix C. In most cases, a ±50°C temperature control is adequate, provided the minimum temperature is not exceeded. The soak time is somewhat more sensitive for mixes containing glass and for high-purity alumina bodies (above 99-percent alumina), although the molybdenum-manganese mixes are insensitive for several hours. In general, the sensitivity to sintering conditions increases with the purity of the alumina body, requiring more precise controls as the alumina content approaches 100 percent. No firm rules have been established, because the variety of mixes employed reacts differently under various conditions. After cooling below 50°C in the furnace cooler, the metallized ceramics are removed from the boat, using plastic- or ceramic-coated tools and/or finger cots or gloves.

4-4. EVALUATION OF METALLIZING

The metallized area can be evaluated by the following simple scratch test. A new, single-edge razor blade is held at approximately 45 degrees to the surface of the sintered metallizing. The blade is then pressed against the surface and forced into the metallizing, while observing the procedure through a 10-power microscope.

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Poor Coating - The metallizing is too soft (usually resulting from under-sintering in time and/or temperature) if the razor blade cuts into the metallizing and peels it, exposing ceramic beneath the surface.

Good Coating - Adequate sintering and metallizing is indicated if the razor blade on subsequent passes over the same place causes a metallic polished spot to appear without removal of metallizing.

A note of caution—be certain with metallizing mixtures containing glass that the polished surface is not the razor blade being rubbed off on excess glass in the metallizing surface, which can give a false indication. Also, this excess glass covers the metallic surface of the metallizing and will permit deposition of electroplating at later stages of the process, with subsequent failure during brazing, because the plating and brazing will not wet the glass-rich surface.

If the metallizing is soft, it can be resintered at a slightly higher temperature and/or a longer period of time, but it is generally advisable to resinter under the same conditions for a second cycle equal to the first. For hand application, it is desirable to apply two or three thin coats of metallizing, with sintering between each coat so that variations in the painting operation can be leveled out on subsequent layers. Application by spraying and roller coating are uniform and can be limited to one layer.

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The thickness of the final metallized ceramic should be between 0.0004 and 0.0015 inch. Thin areas, as low as 0.0002 inch, are acceptable, providing bond and texture are good and the thin areas do not exceed 20 percent of the length of the metallized seal (leak path direction). Local areas as thick as 0.002 inch are acceptable providing the aggregate length of these spots does not exceed 20 percent of the length of the metallized area.

4-5. ELECTROPLATING

After the final sintering, the ceramics are electroplated. The plating serves two functions:

- It protects the metallizing from excess penetration by the solder. If the solder is allowed to be molten for extended periods of time (exceeding one-half hour), it will penetrate the metallizing coating and lift it away from the ceramic, causing leaks.

- It prewets the surface of the metallized layer so that the solder employed during the braze will flow properly and make the joint.

A nickel plate followed by a thin copper plate is generally employed. The nickel forms a barrier against penetration. The copper visually indicates the presence of electroplated conductive surfaces and aids in the flow of most

brazing materials, such as the more commonly employed OFHC copper, copper-gold alloys, or copper-silver alloys. Appendix D lists the melting data for these brazing materials. Typical plating procedures and the recommended plating bath compositions are given in Appendix E. Accurate thickness control of the plating is essential for dimensional considerations, as well as for maintaining a barrier against solder penetration.

The electroplated metallized ceramics and the electroplated metal members are now prepared for the assembly operation. The parts should be stored in clean polyethylene bags in a heated cabinet to minimize oxidation from humidity and airborne sulphides. Contamination control in the use of plastic-coated nylon gloves and/or finger cots is essential to prevent stains on the surfaces to which the seal will be made. Otherwise, there will be subsequent reduction of seal length and an over-all loss of reliability in the assembly, if not initial failure due to a vacuum leak. An oxide imprint, resulting from the acids of finger oils, will act as a stopoff barrier preventing the flow of the molten solder.

SECTION V

FIXTURES AND ASSEMBLY

Cleanliness and contamination control
have been emphasized throughout this manual.
The practice is equally important regarding
fixtures and assembly. All fixtures and jigs
used to assemble the seal must be thoroughly
cleaned to avoid contaminating the parts with
materials which would impede the flow of
solder during the brazing operation. A vapor
degreasing and deionized water rinse are
adequate to remove most organic materials.

Fixtures can be constructed of greened
or oxidized stainless steel, electronic-grade
graphite, or ceramics such as the machinable
lavas and boron nitride. If possible, within the
design requirements of the seal assembly, self-
jigging features should be employed.

In the manufacture of r-f window assem-
blies, it is desirable (because of r-f conduc-
tivity) to construct the outer metal member of
copper. Restraining bands must then be used
to prevent the sleeve from expanding and allow-
ing an excessive gap between the metal and
ceramic member, resulting in improper brazing
and poor fillets. These can be made of several
thin bands of greened stainless steel, restrained
with 0.020- to 0.030-inch molybdenum wire
twisted together in the form of rings holding the

stainless steel bands in place. Alternatively, a single-layer winding of 0.005-inch molybdenum wire provides a more uniform restraint and minimizes puckering at the twist points. With all restrained assemblies, it is desirable to electroplate 0.0005 inch of copper on the brazing site (on either the ceramic or metal member) to ensure having solder penetrate along the seal length. Overrestraint will prevent an adequate flow of solder into the joint, resulting in a weak bond.

Magnesium oxide is recommended as a stopoff when the flow of solder along the metal member must be inhibited. It is easily applied by spraying or brushing, and being extremely refractory, effectively prevents wetting by the brazing metal. The oxide is removed from the assembly by dissolving it in a 5-percent acetic acid solution, followed by several deionized water rinses. Other commonly used stopoffs — such as chrome oxide, aquadag, and alumina dispersions — are to be avoided as they are difficult to remove and may contaminate the device if not completely eliminated.

The fixtures should be designed so that the ceramic member is not exposed to the sudden heat of the furnace. It should be protected by a cover, thus allowing uniform heating of the whole assembly. Ceramic windows and other structures can shatter, even though preheated, when exposed to the hot zone of the furnace because of the intense radiant heat produced in this zone. The thermal inertia of the fixture should be such that thermal shock is

not a problem. However, caution should be used in overcompensating for thermal shock, because an excessively high thermal mass will allow the brazed joint to remain at the melting temperature for a period of time much greater than is scheduled for the hot zone. Extended periods of time at the brazing temperature may damage the seal by dissolving or penetrating the metallizing excessively and weakening the bond at the interface.

SECTION VI

BRAZING

Brazing can be accomplished with a push-through horizontal furnace, belt furnace, or bell-jar brazing. The brazing schedule must account for the heating rate of the assembly, so that the ceramic members are not thermally shocked. It is desirable to preheat the assembly to approximately 50°C below the melting point of the solder. This allows the metal and ceramic members to come to thermal equilibrium and attain the proper gap relationship as planned in the original design. After the thermal soaking below melting temperature, a short excursion into the melting range and back down again, in as brief a time as possible, allows a good flow with a minimum of penetration of the metallizing and alloying with the metal members.

The sensitivity to the brazing time and temperature depends upon the brazing material and the metal member. With copper-gold eutectic alloys being brazed to copper members, an extended brazing time and temperature will allow erosion of the copper member and possible freezing of the solder joint. Nickel plating of metal members which are components of eutectic brazing materials will minimize this alloying effect. Although the alloying effect is damaging on initial brazes, it can be

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successfully employed in attempting reworks
of assemblies which leak upon first brazing.
Adding a small piece of brazing alloy to the
area where the leak is detected will enable a
seal to be made at the brazing temperature
without disturbing the surrounding brazed
areas; the solution of some of the metal mem-
ber sufficiently raises the melting point of the
first brazed joint to prevent it from reliquefying
and disturbing the alignment of the original seal.
Through careful temperature monitoring, two
successive brazes on the same assembly with
the same brazing material can be effected with
this technique. Subsequent step brazes can then
be employed with brazing materials having
prqgressively lower melting points.

After brazing, a helium mass-spectrometer
leak detector is used to check the hermetic seal
for vacuum tightness. At the maximum sensitiv-
ity of most commercial leak detectors (10^{-10}
atmosphere cc per second), minute leaks are not
readily detectable; devices being stored could
then fail because of a gradual rise of the pres-
sure above the minimum operating level.
Equipment to measure extremely small leak
rates due to a pressure rise can be employed.
A penetrating leak check dye has been success-
fully used in many large-scale operations in
which hundreds of seals have been simultaneously
checked. The sensitivity to submicroscopic
leaks is somewhat limited, but the leaks in the
helium mass-spectrometer range can be detected
with careful techniques.

SECTION VII

CONTROL TESTING

A moderately severe test of the completed hermetic seal is thermal cycling to some temperature slightly above the maximum temperature at which the device will be used. This can be repeated several times with helium mass-spectrometer leak checks after each cycle. The first or second cycle will usually eliminate the majority of substandard seals, but there is no clear correlation between additional cycles and the degree of reliability of the seals in the population being tested. All testing, if possible, should be performed on representative samples of units being manufactured and should simulate conditions similar to the end use. For parts of electronic tubes which are to be subsequently brazed to metal members by induction or resistance heating one end of the assembly, testing should duplicate these uneven stresses applied to the seal. Thermal shock, below the level which would cause the ceramic to fail, can be employed to test small, bead coaxial antenna seals. Pressurization of thin ceramic windows has been used to stress the seal area.

ASTM samples are not recommended as a precise indication of the reliability and quality of seals belonging to a population of which the ASTM members were a part. The present ASTM test has been found to have a large coefficient of

variation due to many uncontrollable variables; differences in seal strength which may occur from lot to lot in the metallizing and brazing operations tend to be masked. Coefficients of variation from 25 to 35 percent were observed in the study program on which this manual is based. A modification employing a metal member brazed to one-half of an ASTM set is more desirable and more representative of a typical metal-ceramic seal.

Statistically sampling quantities of manufactured seals which are subjected to destructive testing is also indicative of variations from batch to batch. The destructive testing can be accomplished by tearing the ceramic and metal member apart in a reproducible fashion. For example, with coaxial antenna assemblies, extremely sensitive monitoring is possible by pulling the center coaxial lead while restraining the outer conductor until the ceramic bead fractures. A more sensitive indication of seal quality is obtained by simultaneously monitoring the hermetic tightness of the seal during the application of stress.

SECTION VIII

FAILURE ANALYSIS

It is desirable to evaluate seals which have
failed to determine the cause of failure. A
direct approach is the use of a penetrant dye
which carbonizes after air-firing. This leaves
a carbon track which can be traced through sub-
sequent sectioning and polishing operations.
An even more direct and simpler approach is
peeling the metal member from the ceramic
member, and observing the condition of the
peeled interface. It is difficult to ascertain the
quality of a seal from the condition of the peeled
interface on a new ceramic metallizing com-
bination. However, considerable experience
with various combinations of ceramics and met-
allizing mixtures will enable a trained operator
to detect differences in the degree of sintering,
the thickness of the metallizing, and the site of
the failure—whether at the metal-ceramic inter-
face, metallizing striation, or metallizing-
electroplating interface.

The adage that pulled ceramic indicates a
good seal is not true for all cases of ceramic-
metallizing combinations. The high alumina
ceramics (above 99-percent alumina) with met-
allizing mixes containing glass-forming ingre-
dients (such as silica and calcia) generally peel
clean from the ceramic when they fail, giving the
appearance of a poor bond; but many seals of this
appearance have withstood the most severe en-
vironmental conditions imposed upon them.

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APPENDIX A

RECOMMENDED TOLERANCES AND METALLIZING ALLOWANCES

A-1.   OD SEALS MORE THAN 0.150 INCH OD TO THIN-WALL SLEEVES

Metal Tolerance: ± 0.001 inch

Ceramic Tolerance: ± 0.001 inch

Metallizing Allowance: 0.006 inch on a diameter figured on the *mean* from ceramic and metal sizes *plus* the amount of plate in thousands if metal is plated prior to sealing.

Example: A ceramic with OD of 0.200 ± 0.001 inch is to be sealed into a metal which is to receive 0.001 inch thickness of plate prior to sealing. The machined metal will be 0.200 + 0.006 + 0.002 inch for a final size of 0.208 ± 0.001 inch.

A-2.   OD SEALS, LESS THAN 0.150 INCH OD TO THIN-WALL SLEEVES
Same as Case A-1, except metallizing clearance to be 0.004 inch.

A-3.   ID SEALS MORE THAN 0.150 INCH ID TO THIN-WALL SLEEVES
Same as Case A-1.

A-4. ID SEALS LESS THAN 0.150 INCH ID TO THIN-WALL SLEEVES

Metal Tolerance: ± 0.0005 inch

Ceramic Tolerance: ± 0.002 inch

Metallizing Allowance: 0.005 inch and 0.007 inch figured on the *mean* from ceramic and metal sizes.

Example: A ceramic with ID of 0.045 ± 0.002 inch will require metal sleeves to be specified at 0.038 ± 0.0005 inch and 0.040 ± 0.0005 inch. The closest fitting sleeve is used in assembly.

A-5. ID SEALS TO SOLID PINS

Metal Tolerance: ± 0.0005 inch

Ceramic Tolerance: ± 0.002 inch

Metallizing Allowance: 0.004 inch, 0.005 inch, 0.006 inch, 0.007 inch, 0.008 inch figured on the *mean* from ceramic and metal sizes.

Example: A ceramic with ID of 0.045 ± 0.002 inch will require pins specified at 0.037 inch, 0.038 inch, 0.039 inch, 0.040 inch, 0.041 inch (all ±0.0005 inch). The closest fitting pin is used.

A-6. METALLIZED CERAMICS

Design as described above, but metallizing thickness is 0.0015 inch minimum.

APPENDIX B

METALLIZING MIXTURES

Mixture	Composition
Standard Mo-Mn Mix	240 grams Mo
	60 grams Mn
Active Metal Mo-Mn Mix (65C)*	294 grams Mo
	6 grams Ti
Lithium Molybdate Mix (91B)	270 grams Mo
	30 grams $LiMoO_3$
Calcia Mix (72C)	295.2 grams Mo
	18.4 grams CaO_2
Glassy Mix (50B)	290 grams Mo
	24 grams SiO_2
	11 grams Mn

*Parenthetical references designate Sperry mix numbers. Refer to *Final Technical Report, Metal-Ceramic Seal Technology Study and Final Technical Report, Ceramic-Metal Seals for High-Power Tubes,* furnished by Sperry Gyroscope Co. to U.S. Air Force under Contracts AF30(602)-2047 and AF30(602)-2371, respectively.

APPENDIX C

COMBINATIONS OF CERAMIC BODY, METALLIZING MIXTURE, AND SINTERING CYCLE

		Recommended Sintering Cycle	
Alumina Body	Mix (see Appendix B)	Tempera- ture (°C)	Time at Heat (hours)
94% AD-94	Standard	1500	4-8
94% AD-94	91B	1500	6
94% AD-94	65C	1500	4
96% AL-300	65C	1500	4
96% AL-300	72C	1575	4-8
99.5% AD-995	50B	1575	4-8

Atmosphere: Dissociated ammonia with a dew-point greater than 30°C.

APPENDIX D

BRAZING MATERIALS

Material	Brazing Temperature
Silver-Copper Eutectic*	790°C
37.5% Gold, 62.5% Copper Alloy	1030°C
Copper (OFHC)	1100°C
Silver	980°C

Stopoff: Milk of magnesia; dry thoroughly before firing.

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*Kovar must be nickel-plated to prevent intergranular penetration.

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APPENDIX E

TYPICAL PLATING BATHS
AND PROCEDURES

E-1. QUALITY OF PLATE

Platings should be smooth, continuous, uniform in appearance, and not coarsely crystalline. Pin holes, blisters, modules, pits, indications of "burning", and other harmful defects should not be present. All details of workmanship should conform to the best plating practices.

For a simple quality test, fire the plated item for 10 minutes at 900°C in hydrogen or dissociated ammonia. The plate should show no blisters or separation from the basis metal at the interface when examined at a magnification of approximately 4X.

E-2. COPPER PLATING BATH (ROCHELLE)

a. Equipment

1. *Tank* - Steel, or sulfur-free rubber-lined steel, provided with stainless-steel heating coils, proper temperature controls, and an exhaust hood.

2. *Anodes* - Pure cast copper, with the exception of 5 percent of the anode area which

should be made of steel. The total anode area should be at least twice the cathode or work area.

3. *Power Supply* - Adjustable 0-6 volts dc, with an accurate ammeter of proper range for work size (depends upon work area plus bare rack area).

b. Plating Bath

1.. *Composition*

Sodium Carbonate	4.0 oz/gal
Sodium Cyanide	4.5 oz/gal
Copper Cyanide	3.5 oz/gal
Rochelle Salt	6.0 oz/gal
Free Sodium Cyanide	0.75 oz/gal
Temperature	65°C ± 5°C
pH	12.0-12.8

2. *Preparation*

(a) Dissolve sodium carbonate and sodium cyanide in warm distilled or deionized water.

(b) Add copper cyanide slowly, while stirring the solution.

(c) When the copper cyanide is completely dissolved, add the rochelle salt.

(d) Purify the bath at low current densities for 10 to 12 hours before use. Use a large stainless-steel plate run at 2 amperes per square foot.

3. *Maintenance*

(a) Weekly chemical analyses for the purpose of adjusting the composition to correct concentration.

(b) Daily addition of deionized or distilled water to account for losses (solution evaporated or carried out of tank on work and rack).

(c) Frequent or continuous filtering through activated charcoal filters to remove organic and particulate contamination.

c. *Plating Procedure*

1. Immerse metallized ceramic parts in plating bath for 30 seconds with no current flowing. Apply current and plate at 20 amperes per square foot for 30 seconds, or until a uniform copper film covers the part.

2. Cleaned metal parts are given a 2-percent sodium cyanide dip prior to plating at a current density of 15-40 amperes per square foot. The plating rate at 15 amperes per square foot is 0.0012 inch per hour, and at 40 amperes per square foot is 0.002 inch per hour.

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E-3. NICKEL PLATING BATH (SULFAMATE)

a. Equipment

1. *Tank* - Rubber-lined steel tank or equivalent equipped with a Karbate or tantalum steam coil. Stainless-steel (300 series) or inconel steam coils can be used when the bare metal cannot become anodic. Means for agitating the work and continuous filtrations of the solution are recommended.

2. *Anodes* - 99-percent rolled, depolarized nickel. The anodes should be properly bagged and at least twice the work area.

b. Plating Bath

1. *Composition*

Nickel Sulphamate	60 oz/gal
Boric acid	4 oz/gal
Anti-pit agent SNAC (Barrett Chemical Products Co.)	0. 05 oz/gal
Temperature	50°C
pH	3. 5-4. 5
Density (Baumé)	29-31

2. *Preparation*

Dissolve all salts in warm water with stirring.

3. *Maintenance*

   (a) Weekly chemical analyses for the purpose of adjusting the composition to correct concentration.

   (b) Weekly (or more frequent) filtering through activated charcoal.

   (c) Daily check of pH.

c. *Plating Procedure*

   1. After plating metallized ceramics with copper as in paragraph E-2, immediately rinse in deionized water.

   2. Electroplate in nickel plating tank at 50 amperes per square foot. Plating rate is approximately 0.003 inch per hour.

   3. For metal parts, "strike" first in following bath at 65 amperes per square foot for 1 minute:

Nickel Chloride	32 oz/gal
Hydrochloric Acid 20° Be (tech grade)	4.8 av oz/gal
Room temperature	
99-percent nickel anodes	

      Follow immediately with step 2 above.